

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 November 2001 (29.11.2001)

PCT

(10) International Publication Number
WO 01/89721 A1

- (51) International Patent Classification⁷: **B05D 7/24**, C09K 21/14
- (21) International Application Number: PCT/EP00/04914
- (22) International Filing Date: 25 May 2000 (25.05.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicant (for all designated States except US): **EURO-PLASMA N.V.** [BE/BE]; De Bruwaan 5D, B-9700 Oudenaarde (BE).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **VANLAN-DEGHEM, Anthony** [BE/BE]; Wolvenstraat 29, B-9700 Oudenaarde (BE). **GREGER, Ralf** [DE/BE]; Galgestraat 12, B-9700 Oudenaarde (BE). **PALMERS, Johan** [BE/BE]; Rue Vertbreucq 13, B-7750 Amougies (BE).
- (74) Agent: **LEHERTE, Georges**; K.O.B. n.v., Kennedypark 31c, B-8500 Kortrijk (BE).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/89721 A1

(54) Title: PLASMA POLYMER COATINGS

(57) Abstract: The invention relates to the use of a plasma polymer coating as a fire and/or flame retardant coating on the surface of natural and/or synthetic organic materials. The coating results from exposing the surface to plasma of a monomer vapour, in particular of monomers containing halogen and/or phosphor and/or nitrogen and/or silicon, such as fluor containing compounds, phosphor containing compounds, silicon containing compounds, nitrogen containing compounds. The coating can be applied on equipment like windows, textiles, carpets, etc. used in public areas like aircrafts, cinemas, cars, trains, restaurants, etc., by exposing the surface to plasma at a pressure ranging from 10 to 1200 mtorr, for an exposing time length ranging from 30 seconds to 5 hours. The invention also relates to the method of applying the plasma coating and to objects having a fire and/or flame retardant plasma polymer coating.

PLASMA POLYMER COATINGS

The invention relates to polymer coatings resulting from
5 exposing a substrate to plasma polymerization, and in
particular to such coatings which provide a protective
layer at the surface of the substrate.

Plasma polymerization is a process by which a thin layer
10 of polymeric film is deposited on any surface which is in
contact with the plasma of the organic monomer.
Depending on the deposition conditions, referred to as
the plasma parameters e.g. power, pressure, flow rate,
etc., the properties of the film can be adapted to the
15 requirements.

The film is formed at the face surface of a substrate
from polymerizable species introduced into a plasma-
forming gas. The starting material monomers interact
20 with energetic species, such as electrons, ions or
photons, in the gas phase, consequently effecting the
breaking of chemical bonds and thus creating free
radicals, that then are absorbed at the surface of the
substrate, and bond together and polymerize.

25

Plasma polymerization is a technique that is frequently
used for applying a protective layer or film on surfaces,
for instance to avoid abrasion or crazing of the surface.

30 U.S. patent n° 5,569,497 discloses a process for the
deposition of a layer or of a protective film onto the

surface of a plastic substrate via plasma polymerization. The process comprises a stage of pretreatment of the plastic substrate wherein the substrate is subjected to a plasma established in a reactor under primary vacuum by electrical discharge in a gaseous medium.

U.S. patent n° 4,096,315 gives a description of a method for providing an anti-abrasion coating for a plastic lens. The substrate is firstly exposed in an evacuated plasma polymerization reactor chamber to a first plasma that forms hydroxyl groups on the lens surface, which is believed to allow good adherence qualities of coatings. The reactor chamber is then evacuated. Subsequently, the substrate in the reactor chamber is exposed to a second or monomer plasma for a predetermined time and at a predetermined pressure. The substrate is finally removed from the reactor chamber.

WO 97/31034 describes a method for reducing crazing in plastics material, preferably transparant plastics material where visual clarity is important, which comprises the steps of firstly cleaning the surface by any method which leaves the surface substantially free of any contamination capable of interfering with the adhesion of the plasma polymer coating, and subsequently exposing the cleaned surface to plasma of a monomer vapour as to produce a substantially non-oxidising plasma polymer coating on the surface.

Whereas plasma polymerization is thus known, per se, for providing coatings on various substrates, and in

particular for providing certain protective properties to the surface of plastic materials, it has now been found that certain plasma polymer coatings can be used, in particular, to provide fire retardant and/or flame
5 retardant properties to the surface of organic materials in general.

The subject matter of this invention is therefore the specific use, as a fire and/or flame retardant coating on
10 the surface of natural and/or synthetic organic materials, of a plasma polymer coating resulting from exposing said surface to plasma of a monomer vapour.

For this specific use according to the invention the plasma polymer coating results more in particular from a
15 monomer or mixture of monomers containing halogen and/or, phosphor and/or nitrogen and/or silicon, preferably from precursor gas(es) or liquid(s) selected from fluor containing compounds, phosphor containing compounds, silicon containing compounds, and nitrogen containing
20 compounds .

Particularly suitable halogen containing precursors are for instance CF_4 , C_2F_6 , C_3F_8 , C_3F_6 , C_4F_8 , C_5F_{12} and C_6F_{14} , and other saturated or unsaturated fluorocarbons and
25 hydrofluorocarbons.

Particularly suitable phosphor containing precursors are for instance trimethylphosphate, triethylphosphate and tripropylphosphate and other phosphoric acid derivatives.

Particularly suitable silicon containing precursors are for instance hexamethyldisiloxane (HMDSO), polymethylsiloxane, tetraethoxysilan (TEOS), tetramethylsilan.. (TMS) and the like.

5

Particularly suitable nitrogen containing precursors are for instance ethylamin, triethylamin, allylamin, acrylonitrile and the like

10 For the specific use according to the invention, the plasma polymer coating will preferably result from exposing the surface of the substrate to be treated to the preferred plasma species at a pressure ranging from 10 to 1200 mtorr, for an exposing time length ranging
15 from 30 seconds to 5 hours.

According to a further aspect of the invention, the plasma polymer coating is more particularly used for equipment, like plastic windows, textiles, carpets, wall
20 coverings, furniture, etc., used in public areas, in particular for equipment for aircrafts, cinemas, cars, trains, restaurants, etc.

The purpose of the coating is to provide sufficient fire and/or flame retardency to increase the available time
25 for evacuation of people from these areas, in case of a starting fire, and even to prevent said equipment from catching fire.

The coatings may very suitably be used on objects made of
30 polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polycarbonate, polyoxymethylene,

polyethylene-terephthalate, polybutylene-terephthalate, elastomers, rubbers, natural or synthetic fibers, etc..

A particularly preferred embodiment of the invention involves the use of a plasma polymer coating resulting from the precursor HMDSO, applied on the surface of a polycarbonate or a polymethylmethacrylate object.

The invention also relates to the method for providing fire and/or flame retardant properties to objects of natural and/or synthetic organic materials, by applying a protective coating on the surface of such objects, by exposing the surface to plasma of a monomer vapour.

The method according to the invention is characterized by the specific precursor monomers used, by the specific substrates treated, and by the specific purpose of the coating prepared.

The specific process steps and operating conditions of the method according to the invention, as well as the typical equipment applied, are well known to those skilled in the art of high frequency (cold) plasma treatment. Reference is made to the general handbooks, publications and patents in this area, in particular to US patent n° 4,096,315 to

Chan, C.M. : Polymer surface modification and characterization

Hanser 1994, ISBN 3-56990-158-9, and to

Terlingen, Johannes Gijsbertus Antonius

"Introduction of functional groups at polymer surfaces by glow discharge techniques", ISBN 90-9005620-3,

the disclosure of which is incorporated here in by reference.

Typically the power supply for the plasma can work for
5 example with 10-400KHz, 13,56 MHz, 27,16 MHz, 2.45 GHz or
other available industrial frequencies. It can also be a
pulse-generator. Typical plasma power depends on the
size of the system and can be from 50 -10000 Watt.

A suitable process pressure range lies between 10 and
10 1200 mtorr.

Typically a pressure of 50-500 mtorr is used.

For the process, the substrate is placed somewhere in the
plasma chamber. Typically it can be placed somewhere
between the electrodes or on one of the electrodes or
15 even in the downstream region of the plasma.

Small pieces are preferably treated in a tumbler system.
Woven and nonwoven fabrics and also fibers can be treated
in pieces or on a roll-to-roll system.

In the process the substrate is placed in the chamber and
20 the chamber is being pumped down to a base pressure of
typically 1 - 200 mtorr. The precursor flow is started
to establish a pressure in the range between 10 and 1200
mtorr. The precursor can also be mixed with other gases
like noble gases, oxygen, nitrogen, carbon dioxide,
25 hydrocarbons, hydrogen or even with other precursors.
Then the plasma is started and the treatment is performed
for a time which can be from 30 seconds up to 5 hours.

The process can involve several steps, during which the
gas mixture, the pressure, the plasma power, etc. are
30 changed. Prior to the coating step(s) an activation
plasma can be applied to the substrate to clean the

surface and obtain a better adhesion of the flame retardant coating.

The invention furthermore relates to objects of natural
5 or synthetic material which have a fire and/or flame
retardant surface coating consisting of a plasma polymer
coating, in particular resulting from a precursor monomer
or a mixture of precursor monomers containing halogen
and/or phosphor and/or nitrogen and/or silicon.

10 Preferred plasma polymer coatings result from a precursor
monomer or a mixture of precursor monomers selected from
fluor containing compounds and/or, phosphor containing
compounds and/or silicon containing compounds and/or
nitrogen containing compounds.

15 Preferred objects according to the invention are those
mainly made of polyethylene, polypropylene, polystyrene,
polymethylmethacrylate, polycarbonate, polyoxymethylene,,
polyethyleneterephthalate, polybutyleneterephthalate,
elastomers, rubbers and natural or synthetic fibers.

20 Most preferred objects according to the invention are
objects mainly made of polycarbonate or poly-
methylemetracrylate, having a plasma polymer coating
mainly resulting from HMDSO as monomer precursor.

25 Further features and specific aspects of the invention, as
well as the use thereof, will become apparent from the
following examples, describing preferred embodiments of
the invention in mor detail. It should be observed that
the specific aspects of these examples are only set forth
30 as an explanation of what is ment in the context of the
above general disclosure of the invention, and should not

be interpreted as a limitation of the scope of the invention as such and as expressed in the claims and the end of this specification.

5 EXAMPLE 1

Method of providing a plasma coating on the surface of aircraft windows to increase their flame retardant properties.

For applying said coating on an aircraft window, made from
10 polymethylmethacrylate or Polycarbonate, the window is placed in the process chamber of a plasma system equipment type CD600 or CD1000, which are manufactured and distributed by EUROPLASMA, Oudenaerde. After pumping down the chamber to base pressure, a gas, for example argon or
15 oxygen is introduced and a plasma is ignited for 2 minutes to preclean and activate the window surface. Afterwards, the chamber is pumped down again and the precursor HMDSO is introduced, mixed with Argon. The plasma is started again. After 5 minutes, the Argon flow is replaced by
20 oxygen flow in 3 steps, thus changing the properties of the coating stepwise.

The complete coating treatment needs 20 minutes.

In case of an accident with a fire starting on the
25 outside, the coating increases the available evacuation time for the passengers to leave the plane, before the fire reaches the the inside of the plane (« burn-through-time »).

30 EXAMPLE 2

Characterisation of the coating properties.

X-Ray Photoelectron Spectroscopy (XPS) was used to characterise the structure and chemical composition of the coating surfaces. Scanning Electron Microscopy (SEM) was used for the coating topography characterisation.

- 5 Atomic Force Microscopy (AFM) was used for the measurement of the thickness of the coating.

EXAMPLE 3

Measurement of the fire retardant properties.

- 10 The fire resistance properties of the objects of example 1 are measured by exposing the treated surface to an open flame and measuring the time, until the object catches fire and/or the flame reaches the backside of the object (« burn-through-time »).
- 15 Fire resistance is measured by means of a small Bunzen brander test and a big bunzen brander to evaluate the resistance against heat of a direct flame and heat generated by a flame on a distance of 30 cm. The tests used are existing tests and a prenorm test for burn
- 20 through evaluation.

EXAMPLE 4

- The coatings can be used for carpets, textiles, wallpapers to increase their inflammability. Said coatings increase
- 25 the evacuation time for public areas like restaurants, discos etc. in case of a fire.

C L A I M S

1. Use, as a fire and/or flame retardant coating on the surface of natural and/or synthetic organic materials, of a plasma polymer coating resulting from exposing said surface to plasma of a monomer vapour.
2. Use of a plasma polymer coating according to claim 1, characterised in that the plasma polymer coating results from a monomer or mixture of monomers containing halogen and/or phosphor and/or nitrogen and/or silicon.
3. Use of a plasma polymer coating according to claim 2, characterised in that the monomer(s) result from precursor gas(es) or liquid(s) selected from fluor containing compounds and/or phosphor containing compounds and/or silicon containing compounds and/or nitrogen containing compounds
4. Use of a plasma polymer coating according to claim 3, characterised in that the monomer(s) result from precursor(s) selected from CF_4 , C_2F_6 , C_3F_8 , C_4F_{10} , C_5F_{12} and C_6F_{14} or other saturated or unsaturated fluorocarbons or hydrofluorocarbons.
5. Use of a plasma polymer coating according to claim 3, characterised in that the monomer(s) result from precursor(s) selected from trimethylphosphate,

triethylphosphate and tripropylphosphate or other derivatives of phosphoric acid.

- 5 6. Use of a plasma polymer coating according to claim 3, characterised in that the monomer(s) result from precursor(s) selected from hexamethyldisiloxane (HMDSO), polymethylsiloxane, tetraethoxysilan (TEOS), tetramethylsilan (TMS) and other siloxanes or silanes.
- 10 7. Use of a plasma polymer coating according to claim 3, characterised in that the monomer(s) result from precursor(s) selected from ethylamin, triethylamin, allylamin, acrylonitrile and the like
- 15 8. Use of a plasma polymer coating according to any one of the preceding claims, characterised in that the plasma polymer coating results from exposing said surface to plasma at a pressure ranging from 10 to 20 1200 mtorr, for an exposing time length ranging from 30 seconds to 5 hours.
- 25 9. Use of a plasma polymer coating according to any one of the preceding claims, for equipment used in public areas like aircrafts, cinemas, cars, trains, restaurants, etc.
- 30 10. Use of a plasma polymer coating according to claim 9 for aircraft windows.

11. Use of a plasma polymer coating according to any one of the preceding claims for objects made of polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polycarbonate, polyoxymethylene, polyethyleneterephthalate, polybutyleneterephthalate, elastomers, rubbers and natural or synthetic fibers.
12. Use of a plasma polymer coating according to any one of the preceding claims, characterised in that the plasma polymer coating results from the precursor HMDSO, applied on the surface of a polycarbonate object or a polymethylmethacrylate object.
13. Use of a plasma polymer coating according to any one of the preceding claims, characterised in that the plasma polymer coating results from the precursor C_3F_6 , applied on the surface of a polycarbonate object or a polymethylmethacrylate object.
14. Use of a plasma polymer coating according to any one of the preceding claims, characterised in that the plasma polymer coating results from the precursor triethylphosphate, applied on the surface of a polycarbonate object or a polymethylmethacrylate object.
15. A method for providing fire and/or flame retardant properties to objects of natural and/or synthetic organic materials by applying a protective coating on the surface of said objects, characterised in

that said coating is applied on said surface by exposing it to plasma of a monomer vapour so as to produce a plasma polymer coating.

- 5 16. Object of natural or synthetic material with a fire and/or flame retardant surface coating, characterised in that the coating consists of a plasma polymer coating resulting from a precursor monomer or a mixture of precursor monomers
10 containing halogen and/or , phosphor and/or nitrogen and/or silicon.
- 15 17. Object according to claim 16, characterised in that the coating consists of a polymer resulting from a precursor monomer or a mixture of precursor monomers selected from fluor containing compounds and/or phosphor containing compounds, and/or silicon containing compounds, and/or nitrogen containing compounds.
- 20 18. Object according to any one of claims 16 and 17, characterised in that the object is mainly made of polyethylene, polypropylene, polystyrene, polymethylmethacrylate, polycarbonate, polyoxymethylene, Polyethyleneterephthalate, 25 polybutyleneterephthalate, elastomers, rubbers and natural or synthetic fibers.
- 30 19. Object according to any one of claims 16 to 18, characterised in that the object is mainly made of polycarbonate or polymethylmetracrylate, and the

plasma polymer coating mainly results from HMDSO or C_3F_6 or triethylphosphate as monomer precursor.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/04914

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B05D7/24 C09K21/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 B05D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 856 380 A (REMBOLD MANFRED ET AL) 5 January 1999 (1999-01-05)	1-3, 5, 8, 9, 11, 14-19
Y	column 4, line 17 - column 5, line 17 column 1, line 53-67 column 6, line 9-13 column 8, line 1 column 9, line 65-67	4, 6, 7, 12, 13
Y	EP 0 985 740 A (PROCTER & GAMBLE) 15 March 2000 (2000-03-15) page 2, line 38-58 page 4, line 26-30 page 3, line 32-35	4, 13
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents:**

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

8 document member of the same patent family

Date of the actual completion of the international search

13 March 2001

Date of mailing of the international search report

20/03/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Stembrouck, I

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 00/04914

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 590 467 A (ROEHM GMBH ; FRAUNHOFER GES FORSCHUNG (DE)) 6 April 1994 (1994-04-06) page 2, line 26-42 page 3, line 4-17, 51-54	7
Y	US 4 778 721 A (SLIEMERS FRANCIS A ET AL) 18 October 1988 (1988-10-18) column 3, line 3-7, 35-39, 47-51 example 1	6, 12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/04914

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5856380	A	05-01-1999	AU 1311895 A WO 9516715 A EP 0734400 A JP 9506678 T	03-07-1995 22-06-1995 02-10-1996 30-06-1997
EP 0985740	A	15-03-2000	AU 6028999 A WO 0014296 A	27-03-2000 16-03-2000
EP 0590467	A	06-04-1994	DE 4232390 A AT 166901 T DE 59308639 D DK 590467 T ES 2118866 T	31-03-1994 15-06-1998 09-07-1998 22-03-1999 01-10-1998
US 4778721	A	18-10-1988	AT 64327 T AU 598829 B AU 7536787 A DE 3770705 D EP 0252870 A GR 3002125 T JP 63033429 A	15-06-1991 05-07-1990 14-01-1988 18-07-1991 13-01-1988 30-12-1992 13-02-1988